

# Predicting Soil and Water Chemistry in and below the Root Zone of Agricultural Lands: Major Ions, Nutrients and Toxic Ions

D.L. Suarez

USDA-ARS, Salinity Laboratory, Riverside, CA [dsuarez@ussl.ars.usda.gov](mailto:dsuarez@ussl.ars.usda.gov)

The focus of ARS research on inorganic chemicals centers around the need to maintain a productive soil environment for crop production while minimizing or avoiding off-site degradation of soil and water resources. The inorganic chemicals of interest are salts, nutrients and potentially toxic ions. Modeling is necessary for predict of the leaching of chemicals under existing practices and more importantly as a management tool to evaluate new practices. Evaluation of practices must of course consider not only chemical discharge but crop productivity and sustainability.

The environment of primary interest is the soil root zone. In some instances groundwater and surface water processes and transport is also of interest. The root zone environment is a dynamic region of the soil with changes in water content, plant uptake of water and chemicals, changing redox and gas phase composition and in many instances short residence times. Chemical modeling is highly dependent on an accurate description of water flow, thus a variably saturated water flow routine is often needed. Plant water uptake is an important component of water flow and determinant of solute composition (evapotranspiration concentrates salts into the remaining soil water). In most instances chemical modeling in the root zone requires modeling of plant water uptake in response to environmental stresses (water, salts, ions, nutrients, and climate). Since the system is dynamic, predictions based on equilibrium (thermodynamic) assumptions will usually not be satisfactory. Additional nutrients ( $\text{NH}_4$ ,  $\text{PO}_4$  and B), and toxic elements (Se, As, B, and Mo, as well as some heavy metals).

## 1 MODELING MAJOR ION CHEMISTRY

### 1.1 *Rationale and processes*

Modeling of major dissolved ions (Na, K, Ca, Mg, Cl  $\text{SO}_4$ ,  $\text{NO}_3$ , and  $\text{HCO}_3 + \text{CO}_3$ ) is necessary for salinity control, primarily for western irrigated agriculture. High salt concentrations reduce crop yield and water consumption. In this instance a plant stress response model is needed to model salt composition and transport. Major ion processes needed to be modeled include mineral precipitation-dissolution, and cation exchange. Minerals of major importance are calcite and gypsum. Since calcite solubility depends on  $\text{CO}_2$  carbon dioxide partial pressure, there is a need to simulate gas concentrations. In some instances it may be sufficient to estimate annual or seasonal gas phase profiles with a fixed boundary condition, in other instances  $\text{CO}_2$  dynamics are important and both production and transport are necessary to predict concentration. Calcite kinetics may need to be considered in some instances or alternatively the mean ion activity product for calcium carbonate is relatively stable for short residence times and is a better predictor than calcite equilibrium (Suarez et al., 1992). Precipitation dissolution of more soluble salts such as mirabilite and halite and generally not necessary since in an agricultural setting these salts would only occur in a dry surface crust and quickly resolubilize after irrigation or rainfall.

## 1.2 Leaching and salinity control

Salinity control in the root zone is a major concern for western irrigated agriculture. Salt leaching must consider soil mineralogy, hydraulic properties, climate, and plant water uptake. Salinization may occur as a result of under irrigation and/or capillary rise from shallow saline ground water. Plant response to salts is not just related to overall salt composition, but to specific ion concentrations as well, thus need be to predict individual ion concentrations.

## 1.3 Sodic soil reclamation

High levels of exchangeable Na, especially when salinity levels are low, results in adverse soil physical properties, including reduction in hydraulic conductivity, adversely affecting water infiltration, aeration and soil tilth. The UNSATCHEM code simulates the effects of pH, salinity and exchangeable Na percentage on hydraulic conductivity, utilizing a modification of the variable saturated water flow equation as follows (Suarez and Simunek, 1996)

$$K(h) = K_s K_r r = K_s r S_e^{1/2} [1 - (1 - S_e^{1/m})^m]^2 \quad (1)$$

where  $K(h)$  is the hydraulic conductivity at the specified pressure head,  $K_s$  is the saturated hydraulic conductivity,  $K_r$  is the relative hydraulic conductivity (scaled),  $r$  is the reduction function defined by the chemistry of the soil solution,  $S_e$  is defined by  $(\theta_w - \theta_r)/(\theta_s - \theta_r)$ , and  $m$  is an empirical parameter. The  $\theta_w$ ,  $\theta_r$  and  $\theta_s$  correspond to the existing, residual, saturation water contents respectively. This is an important consideration for prediction of water flow in saline soils as shown by the results of column experiments, Fig 1 (Suarez et al. 1984)

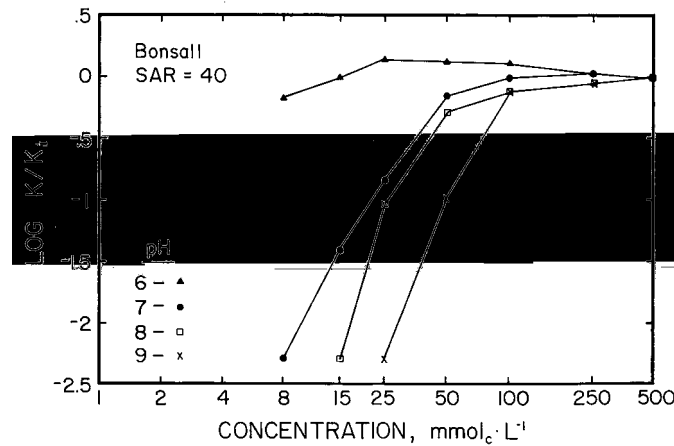


Figure 1 Change in relative saturated hydraulic conductivity as related to solution concentration, SAR and pH.

Figure 2a shows a comparison of predicted versus observed effect of gypsum mixed into the top 15 cm of a saline sodic soil subsequently leached with dilute water (Suarez, 2001). The SAR (sodium adsorption ratio) is directly related to the exchangeable Na percentage (percentage of the cation exchange sites that are occupied by Na). Under enhanced CO<sub>2</sub> production and reduced transport in the gas phase, calcite can be an appreciable source of calcium, suitable for reclamation. The predictions shown in Fig 2b match field observations of reclamation of calcareous soils using this “green manuring” technique.

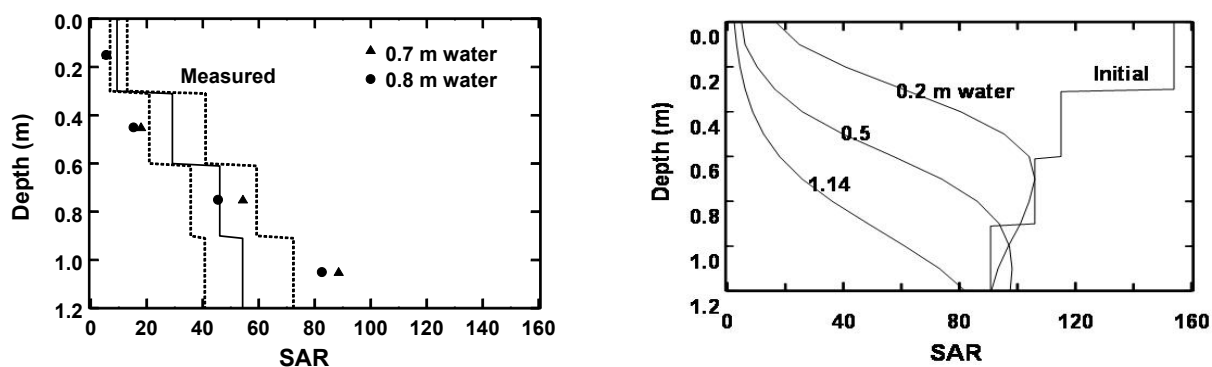


Figure 2 a) Comparison between predicted and observed SAR with depth after application of gypsum and leaching with 0.74 m of water( and b) Predicted change in SAR as related to water applied, utilizing calcite dissolution and management practices to enhance CO<sub>2</sub> concentration in the soil.

## 2 NUTRIENTS

### 2.1 Nitrogen

Nitrate leaching from agricultural soils is a major environment concern. High crop productivity requires high N availability. The RZWQM (Ahuja et al. 1999) contains a chemical routine for cation exchange including NH<sub>4</sub> and N transformations from nitrate, NH<sub>4</sub> and various organic matter N pools in the soil, as well as consideration of ammonia volatilization. ARS needs in this area are primarily to predict the concentration of nitrate leached below the root zone as related to nitrogen applications and management practices (tillage, fallowing fertilizer timing etc.), however knowledge of methane production and losses to the atmosphere are also needed to evaluate greenhouse gas production.

Many nutrient models utilized by ARS do not attempt to model the chemical reactions but rather provide regression type routines to predict nutrient losses. These models are useful but not within the scope of the present topic, process- based chemical modeling.

### 2.2 Phosphorous

In agricultural environments, transport of P is primarily a concern associated with sediment transport, thus mostly associated with physical erosion models rather than chemical reactions. Adsorption/precipitation of P is of interest in as much as it impacts plant P uptake.

## 3 TOXIC IONS

Saline water is often associated with elevated concentrations of B, Se, As and Mo. These elements adsorb to mineral surfaces thus prediction of their concentrations requires adsorption modeling. For Se and As there is also a need to consider redox reactions, volatilization of organic gases and incorporation into organic matter. Chemical modeling is necessary to predict transport. Boron is both an essential plant nutrient and toxic at higher concentrations. Modeling of B adsorption/desorption and transport has been simulated using UNSATCHEM (Suarez and Simunek, 1996.) Figure 3 shows the predictive capability of the model utilizing

the constant capacitance model for adsorption and generalized model parameters (Suarez, 2002).

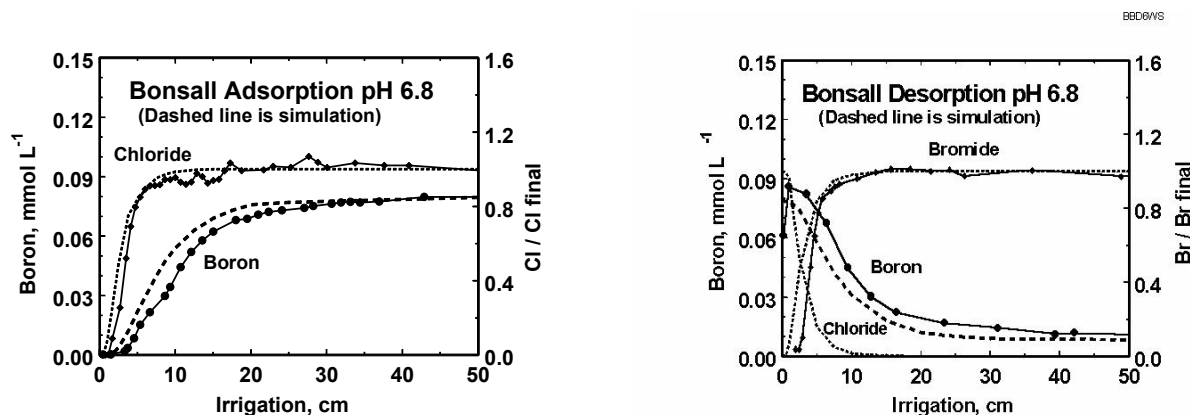


Figure 3 Comparison of UNSATCHEM predictions and column data for a) Cl and B leaching during adsorption and b) CL and B leaching during desorption.

#### 4 HEAVY METALS

Heavy metals are of concern in urban environments as well as former orchards where lead arsenate was used as an insecticide. At present, transport modeling has not been utilized, but would be useful for evaluation of remediation options.

#### 5 REFERENCES

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